



Photocatalytic oxidation of octamethylcyclotetrasiloxane (D4): Towards a better understanding of the impact of volatile methyl siloxanes on photocatalytic systems

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ABSTRACT

Photocatalytic treatment of air, using TiO₂ as the catalyst, is developing more and more because of increasing air pollution which is becoming a serious problem that needs to be addressed immediately. Furthermore Volatile Methyl Siloxanes (VMS) are becoming more and more abundant indoors and in ambient air owing to their increased use in different domain such as cosmetic and personnel care products. Once VMS are present in air, rapid catalyst deactivation can be observed and this reduces the efficiency of the photocatalytic system. In this study octamethylcyclotetrasiloxane D4 was chosen as the VMS model, and its photocatalytic oxidation was investigated. Experiments were performed at various D4 concentrations in synthetic air under 40% relative humidity and D4 conversion was measured using TD-GC-MS analysis, while the TiO₂ surface was analyzed by X-ray photoelectron spectroscopy (XPS). Under these conditions at 250 ppbv of D4, the photocatalytic activity as measured by D4 conversion decreased from 98% to 30% after 3 days of irradiation, thus revealing the deactivation of TiO₂, and total deactivation was observed after three days of irradiation at 500 ppbv of D4. The photocatalysis of toluene was studied under the same conditions over a period of three days and a conversion close to 100% was found without any deactivation, hence leading to the confirmation that only D4 contributes to the deactivation of TiO₂. Additional experiments on a binary mixture of D4 and toluene allowed us to gain a better understanding of the impact of VMS on photocatalytic systems.

For the photocatalytic oxidation of D4, three photoproducts were identified, viz. heptamethylhydroxycyclotetrasiloxane, heptamethyl(hydroxymethyl)cyclotetrasiloxane and hexamethylcyclotrisiloxane. XPS analyses of the media show an increase in Si/Ti ratio and the appearance of a SiOH component, which allows us to better understand the nature of the deposit responsible for the deactivation of TiO₂.

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1. Introduction

Nowadays, people generally spend more than 80–90% of their time in an indoor environment (e.g. home, office, school, and shopping mall), where they can be exposed to a variety of airborne pollutants such as NO_x, CO, volatile organic compounds (VOCs), and particulate matter. To reduce exposure to these pollutants, different technologies have been implemented such as filtration [1], adsorption [2,3] and photocatalytic oxidation (PCO) [4–6]. Although an increasing number of PCO air cleaners have been introduced in the market, the PCO performance is still poorly evaluated due to several reasons and/or limitations:

1. The study of PCO performance under real-life concentrations (ppbv) of indoor pollutants is difficult and requires precise

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measurements using advanced analytical instrumentation. Thus, most PCO studies have been performed using significantly higher orders of concentration (ppmv) of pollutants than those present in reality. Extrapolating the results is not always simple and whether the same performance, mechanisms and products are obtained remains an open question [7,8].

- Indoor air is a complex mixture of pollutants. It is important to thoroughly investigate the kinetics, mechanisms and reaction products for individual VOCs but how the performance of PCO is affected when challenged with a mixture of VOCs [9] remains unclear.
- Relative humidity (RH) is a key parameter influencing the performance of PCO. It is essential to understand how it impacts the reaction rates, mechanisms and products considering the variability of RH in different indoor environments under different climates [8].
- Performance of PCO might degrade over time due to poisoning of the catalyst.

While many studies have been carried out to better understand the first three points, only a few have been devoted to the last one and this is surprising, taking into account that deactivation of the photocatalyst is one of the principal practical problems.

In this context, the main pollutants assessed with respect to a possible deactivation have been ethanol [10], nitrogen containing compounds [11], and volatile methyl siloxanes (VMS) such as tetramethylsilane or octamethyltrisiloxane [12,13]. The photocatalytic oxidation of VMS is limited, Sun et al. studied the decomposition of gaseous phase of octamethyltrisiloxane on TiO_2 , using relatively high concentration levels (about 20 ppmv). Using XPS they identified a layer of SiOx on TiO_2 without identifying any intermediate organic compounds [12]. The photocatalytic oxidation of tetramethylsilane was investigated and no intermediate organic products were found [13].

As stated earlier VMS are more and more frequently found in indoor and ambient air due to their common use in personal care products, deodorants, skin care products and as conditioners in hair care products [14–16]. For example in the United States in 2006, the production volumes of cyclic VMS such as octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) were in the range of 45–225, 22.5–45, and 0.45–4.5 ktons [17], respectively.

Recently volatile cyclic methyl siloxanes were also found in ambient air in three Chinese cities. While D5 was only detected in trace concentrations in a few air samples, hexamethylcyclotrisiloxane (D3) and D4 were, as expected, the dominant compounds found [18].

More recently Lamaa et al. also found that D4 was the most abundant VMS with concentration ranging from 1 to $5 \mu\text{g m}^{-3}$ in ambient air at petrol pump and $1\text{--}20 \mu\text{g m}^{-3}$ indoors in parking [19].

On other hand, some specific models have been developed to predict the atmospheric fate of VMS and their degradation products [20,21] or to estimate the effects of atmospheric aerosols on the fate of airborne VMS [22].

In this context, for a better understanding of the impact of VMS on photocatalytic systems, D4 was chosen as a VMS model compound as it is one of the most important VMS. Its photocatalytic degradation has been followed using advanced analytical methods including thermal desorption coupled to GC-MS (TD-GC-MS), atmospheric pressure chemical ionization (APCI) and GC coupled to pulsed discharge helium ionization detector GC-PDHID for analysis of the gas phase and X-ray photoelectron spectroscopy (XPS) for analysis of the surface. In addition, toluene was chosen as the VOC model, firstly for comparison with D4, and secondly, to evaluate the effect of a mixture constituted of D4 and toluene. Furthermore,

toluene belongs to BTEX, a major group frequently encountered in indoor and outdoor air [8,23,24].

2. Experimental

2.1. Reactor and experimental set-up

Fig. 1 shows a schematic representation of the experimental set-up used for the PCO of D4 and toluene in gas phase. Experiments were conducted in continuous flow mode using an annular flow-through reactor of about 50 mL, made of stainless steel and equipped with an optical Pyrex glass window (transmittance: wavelength $>290 \text{ nm}$), a water cell to prevent overheating and a high pressure mercury UV lamp (HPK 125 W, Philips). The photocatalytic medium was non-woven paper (natural cellulose fiber), coated with TiO_2 PC-500 (100% anatase, BET area: $300 \text{ m}^2 \text{ g}^{-1}$, crystal size: 5–10 nm), SiO_2 is used as a binder for the fixation of TiO_2 particles onto the support, supplied by Ahlstrom, France. A gaseous stream of D4 was generated using a permeation tube from VICI (USA) filled by pure liquid D4 and placed inside a furnace maintained at a constant temperature of 50°C . Nitrogen gas at a constant flow rate of 50 mL min^{-1} was passed over the permeation tube and subsequently mixed with O_2 or N_2 and water vapor (H_2O) at gas flow rates corresponding to target D4 concentration ranging from 50 to 500 ppbv. In all experiments the total flow rate was set at 130 mL min^{-1} . The gas flow rates were adjusted using mass flow controllers in the $0\text{--}1000 \text{ mL min}^{-1}$ range (Brooks, 5850S series). The final gas stream humidity and temperature were measured using a thermohygrometer (Rotonic Hygropalm 1, France).

2.2. Sampling and analysis of gaseous intermediates

During the irradiation experiments, D4 and gas phase reaction intermediates were collected for $2 \text{ min}^{-1} \text{ h}$ at regular time intervals and at a flow rate of 30 mL min^{-1} . Multibed solid sorbent tubes packed with Carbotrap C, Carbotrap and Carboxen 1000 (Supelco) in that order were used to adsorb as much the organic compounds as possible [19]. In preliminary experiments, the sampling conditions were tested against breakthrough by collecting a 600 mL sample of toluene and D4 with two identical tubes connected in series. The analysis showed no breakthrough from the first trap to the second one, confirming that no loss of products occurs during the sampling step (2 min, 60 mL). In addition, the repeatability of the whole analytical procedure (sampling and analysis) was measured and the resulting relative standard deviation was found to be $<3\%$. The analysis of D4 was then performed using TD autosampler series 2 Ultra, thermal desorber Unity Markes, GC 6890 and MS 5973 by Agilent Technologies. The TD was programmed to desorb compounds at 300°C . The desorbed compounds from the tubes were recondensed in the cold trap (set at -10°C), the trap was then desorbed by flash heating up to 320°C , and compounds were injected in to GC-MS with a 10 split ratio. All analytes were quantified using TD-GC-MS multipoint calibration curves developed from pure chemical standards, purchased from Aldrich.

A Varian Select Silanes capillary column (60 m \times 0.32 mm \times 1.8 μm), a special column for organic siloxane compounds, was used for the chromatographic separation of VMS. The oven temperature was initially set at 50°C for 5 min, and heated at a rate of $10^\circ\text{C min}^{-1}$ to 240°C , then maintained at this temperature during 1 minute. The carrier gas flow was set at 1.4 mL min^{-1} and the GC-MS interface was set at 280°C . The EI mass spectrum was obtained for siloxanes with electron energy of 70 eV over a mass range of 30–500 amu. Acquisition mode was set to SCAN/SIM.

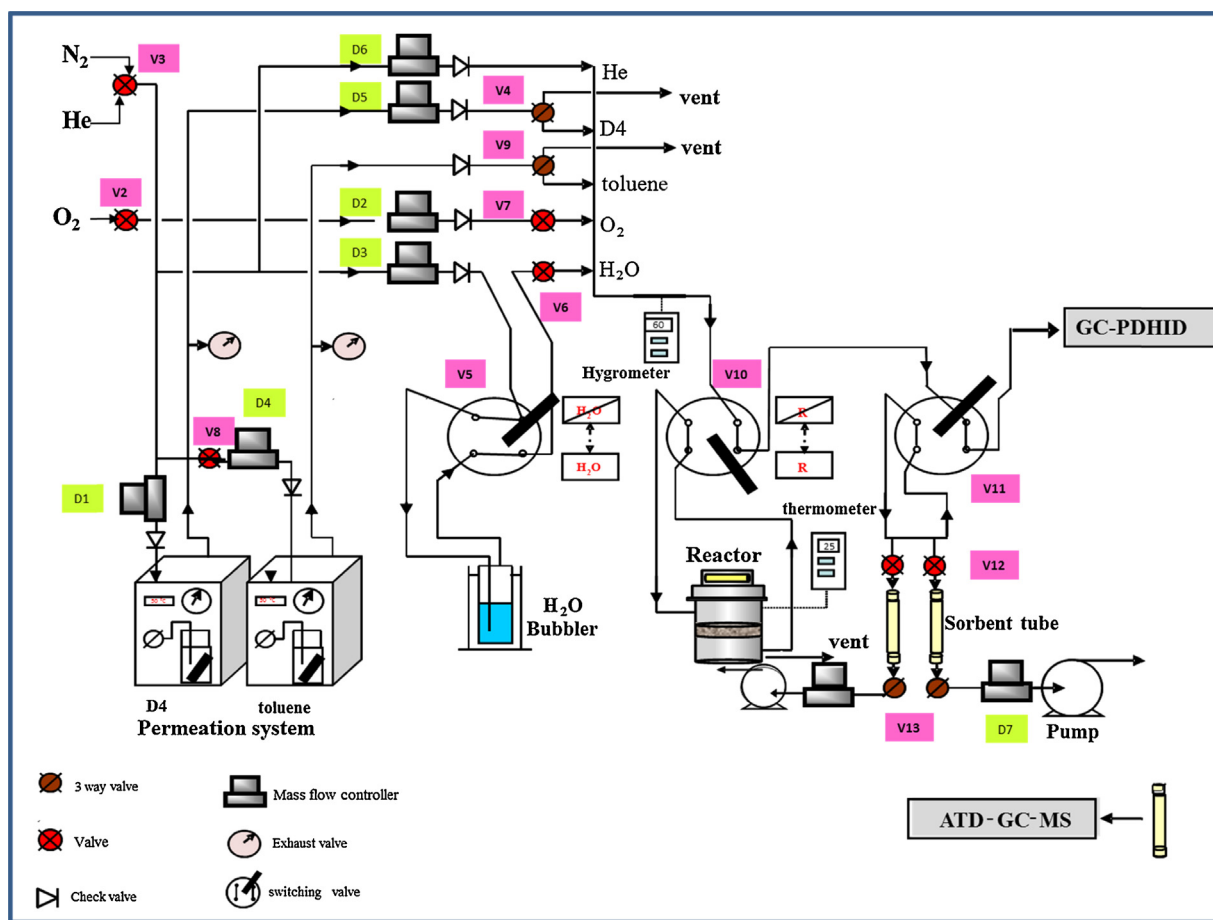


Fig. 1. Schematic representation of the experimental set-up used for the photocatalytic oxidation of D4 and toluene.

Atmospheric Pressure Chemical Ionization (APCI) analysis, which is an ionization method considered a complement to electrospray, generates primarily singly-charged ions and not multiply-charged ions. It was investigated in order to obtain molecular mass data of intermediate compounds, D4 and gas phase reaction intermediates were collected for 3 h at flow rate of 100 mL min^{-1} using activated carbon SKC tube. Desorption was carried out using dichloromethane as the extraction solvent. Samples were then injected directly to APCI.

2.3. Calibration curves

Calibration curves were performed by liquid doping of $1 \mu\text{L}$ of D4 and toluene solutions, using the heated injector port of a conventional chromatograph set at 250°C and a flow of helium set at 60 mL min^{-1} during 4 min. Once prepared the tubes containing the standard solutions were desorbed in the TD as described earlier for the samples. This calibration was used for D4 and toluene.

2.4. On-line measurements of CO/CO_2

The formation of CO/CO_2 during the reaction was monitored every 2 h using a GC-PDHID instrument that consisted of one 10-way Valco valve (V10) equipped with a 1 mL sample loop, two packed chromatographic columns placed in parallel configuration: a Porapack Q (L: 5 m, ID: $1/8''$) and a Tamis 13-X (L: 2 m, ID: $1/16''$) from RESTEK, a D4-I detector (Valco instruments). The carrier gas was pure Helium 6.0 from Linde which was additionally purified by a Valco HP-2 purifier. The oven temperature

was 45°C and column flow rates were 10 mL min^{-1} for Tamis 13-X and 30 mL min^{-1} for Porapack Q. Using these conditions, analysis time was around 5 min. Calibration of CO/CO_2 was carried out using a standard mixture of CO/CO_2 (5 ppmv in He). The detection limits for CO and CO_2 were 40 and 20 ppbv, respectively. The relative standard deviation was 1.2% for CO and 0.9% for CO_2 . For CO/CO_2 measurements, it should be pointed out that synthetic air in the photo reactor was replaced by He/2% Oxygen during all irradiation experiments in order to avoid the overlapping of chromatographic peaks of N_2/O_2 with those of CO/CO_2 during the GC-PDHID analysis. Preliminary experiments were conducted to evaluate the difference when Helium was used instead of N_2 and when only 2% of O_2 was employed. The results showed that the variation of conversion of D4 was negligible.

2.5. Analysis of adsorbed species

TiO_2 surface was investigated after PCO using X-ray photoelectron spectroscopy. XPS analysis was performed on the area of the slides exposed to the UV and D4 to measure the amount of silica that had accumulated on the surface from photocatalytic action. The X-ray source was monochromatised $\text{Al K}\alpha$ ($h\nu = 1486.6 \text{ eV}$), and analyser pass energies: 160 eV for widescans and 20 eV over specific photoelectron peaks applied. Cumulative scans were carried out over each peak and total scan time for each region studied was 5–50 min. All spectra were referenced to the $\text{Ti}2p \ 3/2$ peak fixed at 458.8 eV, representative of TiO_2 present in the catalyst.

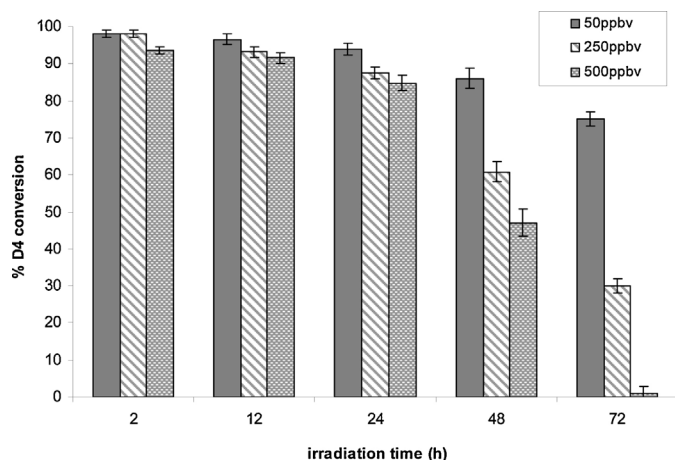


Fig. 2. Influence of concentration on the conversion (%) of D4 (RH: 40%).

3. Results and discussion

3.1. Photocatalytic oxidation of D4

Preliminary blank experiments were conducted: in the absence of photocatalytic media under UV irradiation and in the dark in the presence of the photocatalyst. Results show that there is no degradation of D4 in absence of photocatalytic media under UV irradiation. In dark the loss in D4 concentration due to its adsorption on the photocatalytic media is very negligible compared to the loss due to the photocatalytic degradation.

Experiments were performed at different D4 concentrations in synthetic air under 40% of relative humidity. Inlet concentration was set at 50, 250 and 500 ppbv in order to determine the influence of D4 concentrations. Experiments were carried out in triplicate. The conversion of D4 was calculated from the difference between the inlet and outlet D4 concentrations, as follows:

$$\text{Conversion \%} = \frac{[D4]_{in} - [D4]_{out}}{[D4]_{in}} \times 100$$

Fig. 2 shows the variation of conversion of D4 at different concentrations as a function of times. At both 250 ppbv and 500 ppbv of D4, D4 conversion was found to decrease significantly with irradiation time from 98% to 30% and from 98% to less than 1%, respectively, while a less significant decrease was observed at 50 ppbv.

So, for the three tested concentrations, results show that the PCO efficiency decrease after 3 days of irradiation, revealing a deactivation of TiO_2 accompanied by a yellowish coloration of the media which means that D4 concentration affected the photocatalytic degradation efficiency. For the following experiments, D4 photocatalysis was performed at 250 ppbv.

3.2. Photocatalytic oxidation of toluene

In order to further understand the cause of this decreased activity, toluene was chosen as a model VOC. The PCO of 250 ppbv of toluene was performed using the same conditions (flow rate, oxygen and relative humidity) as for D4 experiments.

Fig. 3 shows toluene conversion as a function of irradiation time. Contrary to the results obtained with D4, toluene conversion remains stable at ca. 100% during the three days of irradiation as it was found in a previous study [8].

3.3. Mineralization on-line measurements

The mineralization extent (%) was determined by comparing the concentration of carbon dioxide (CO_2) produced to the theoretical

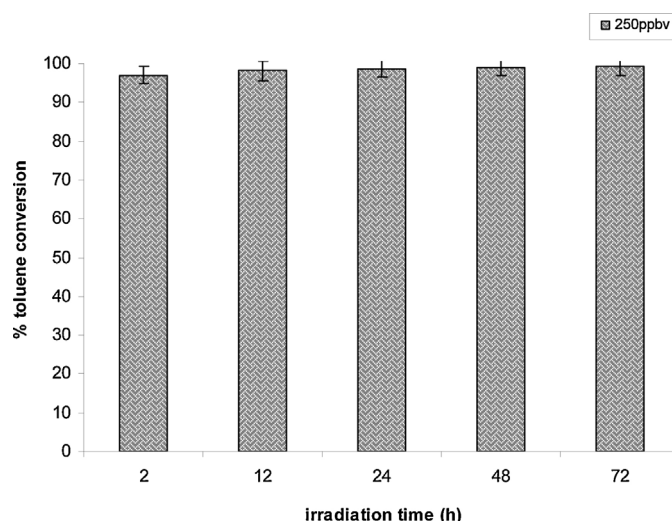


Fig. 3. Conversion (%) of toluene (RH: 40%).

one (if mineralization is complete: 1 mol of D4 should lead to the formation of 8 mol of CO_2), using the following equation:

$$\% \text{Selectivity toward } CO_2 (S_{CO_2}) = \frac{[CO_2]_{measured}}{[CO_2]_{theoretical}} \times 100$$

where

$$[CO_2]_{theoretical} = \frac{8 \times \% \text{conversion} \times [D4]_{in}}{100}$$

Fig. 4 shows that while D4 conversion decreases from 98% to 30% after 3 days of irradiation, the mineralization selectivity toward CO_2 decreases from 65% to 41% with an almost constant value between 48 h and 72 h. Even if the S_{CO_2} of the mineralization seems to be relatively similar for 48 h and 72 h, the number of molecules mineralized decreased since the conversion rate decreases in the same time.

3.4. Reaction products in gas phase

Sun et al. studied the photodegradation of linear octamethyl-trisiloxane but no organic intermediates were detectable in their experimental conditions [12] which consisted of GC with a methanizer and a flame ionization detector and XPS analysis. In the same way, by using electron microprobe (EMP) and XPS analysis Hay

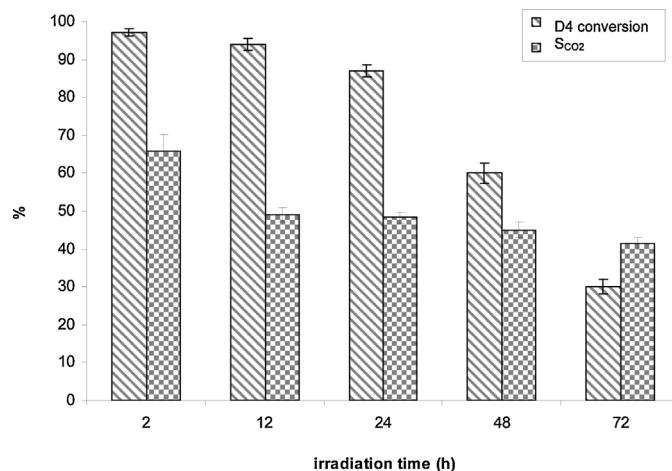
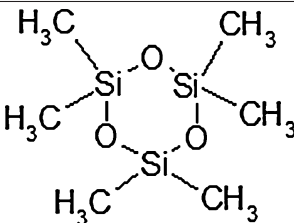
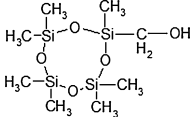
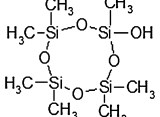
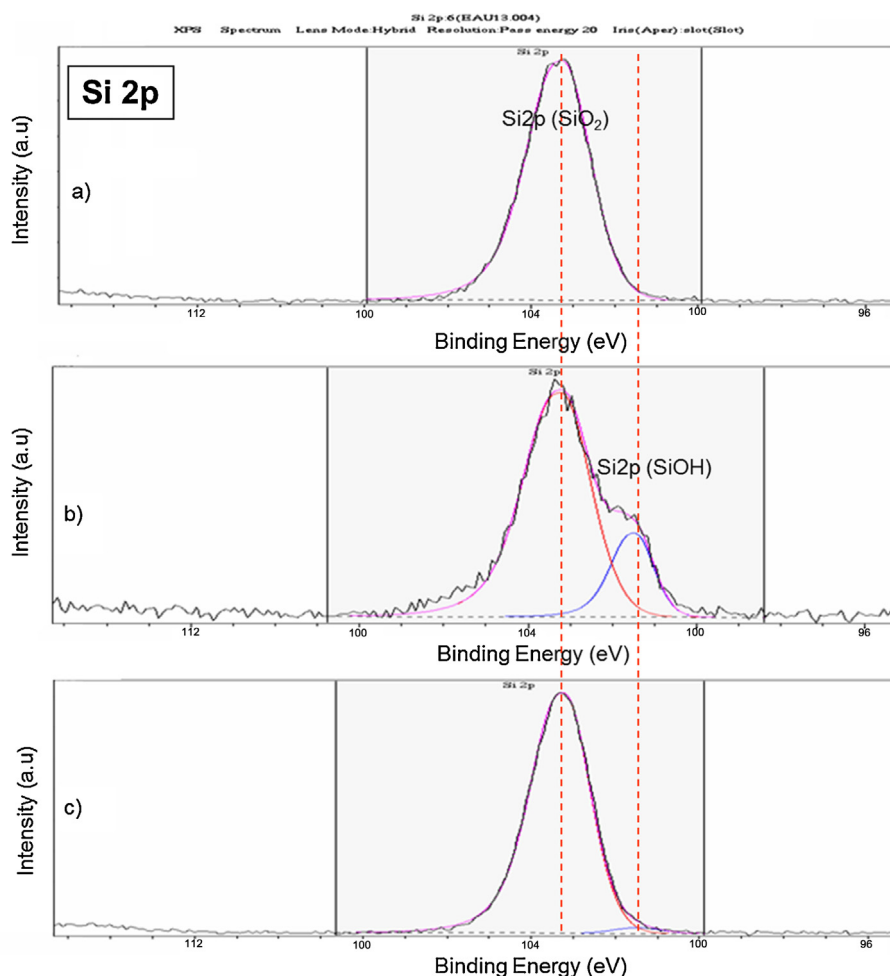


Fig. 4. Comparison of conversion (%) and mineralization represented by S_{CO_2} (%) for D4 (inlet conc 250 ppbv, RH: 40%).

Table 1Mass spectra and data structures of identified intermediates by TD-GC-MS and APCI after irradiation of D4 in presence of TiO₂.

Name	Structure	Retention time (min)	(M+H) ⁺ (APCI)	Fragment ions (EI-MS) (m/z)
Hexamethylcyclotrisiloxane (P1)		11.5	223	207, 191, 177, 96
Heptamethyl(hydroxymethyl)cyclotetrasiloxane (P2)		17.7	313	297, 267, 251, 237, 207, 193, 179, 119, 103, 73, 59
Heptamethylhydroxy cyclotetrasiloxane (P3)		20.3	299	283, 267, 237, 223, 193, 147, 126, 105, 89, 75, 45

**Fig. 5.** XPS spectra for Si 2p region at various times of photocatalysis oxidation of D4: (a) 0 h; (b) 48 h; (c) 72 h.

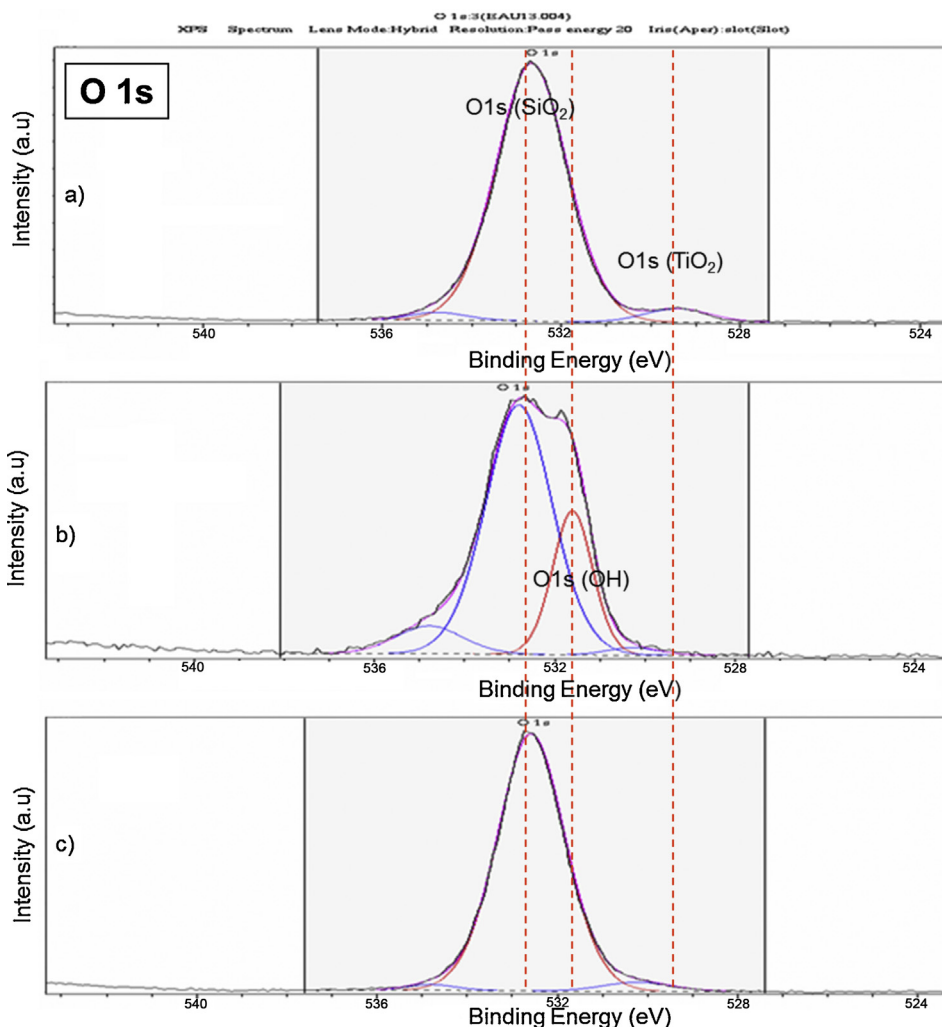


Fig. 6. XPS spectra for O 1s region at various times of photocatalysis oxidation of D4: (a) 0 h; (b) 48 h; (c) 72 h.

et al. did not identify organic intermediates [13] during the PCO of tetramethylsilane.

In our case, by the use of sampling tubes followed by analysis using TD-GC-MS allowed us to identify some intermediates. Indeed, these intermediates were characterized only by some fragments and not by the ion molecular peaks. APCI method was used in order to obtain information of the molecular peak mass value. Using these two methods, three photoproducts were identified during D4 PCO, which are heptamethylhydroxycyclotetrasiloxane, heptamethyl(hydroxymethyl) cyclotetrasiloxane and hexamethylcyclotrisiloxane (D3) as seen in Table 1. Heptamethylhydroxycyclotetrasiloxane and heptamethyl(hydroxymethyl)cyclotetrasiloxane were also identified in a previous study dealing with the photodegradation of D4 with OH radical [25].

3.5. XPS analysis

The analysis of the TiO₂ surface after D4 PCO using XPS could be helpful to find out more about the deactivation mechanism of the catalyst. Table 2 shows the Si/Ti ratio at different times of irradiation and a clear increase in the Si/Ti ratio as a function of the irradiation time is noted, leading to the conclusion that compounds containing silicon were more and more adsorbed on the TiO₂ surface during D4.

Fig. 5 shows the change of the TiO₂ XPS spectra in the Si2p regions before and after irradiation for different periods. The figure shows a spectrum consistent with SiO₂ with binding energy (B.E. = 103 eV) [26] in the blank (only the media, without D4) due to the use of SiO₂ in the photocatalytic media as mentioned before but a new Si 2p component was observed at lower binding energy (B.E. = 101.5 eV) after 48 h of PCO which was attributed to the formation of SiOH. After 72 h of PCO, only the SiO₂ peak at 103 eV remains. This result might be explained by the fact that during irradiation intermediate organic compounds containing SiOH were first adsorbed on TiO₂ surface while after 3 days of irradiation, SiOH adsorbed on the TiO₂ surface becomes progressively oxidized into SiO₂.

Fig. 6 shows the changes in the O1s peak before and after irradiation. Before irradiation two peaks existed, the first corresponds to O1s in SiO₂ (B.E. = 532 eV), and the second one corresponds to O1s in TiO₂ (B.E. = 529.9 eV). After 48 h of irradiation, a new peak (B.E. = 531 eV) was observed which was attributed to the presence

Table 2
Silicon titanium ratio during irradiation of D4.

Irradiation times (h)	Si/Ti
0 h	20.5
48 h	31.7
72 h	39.4

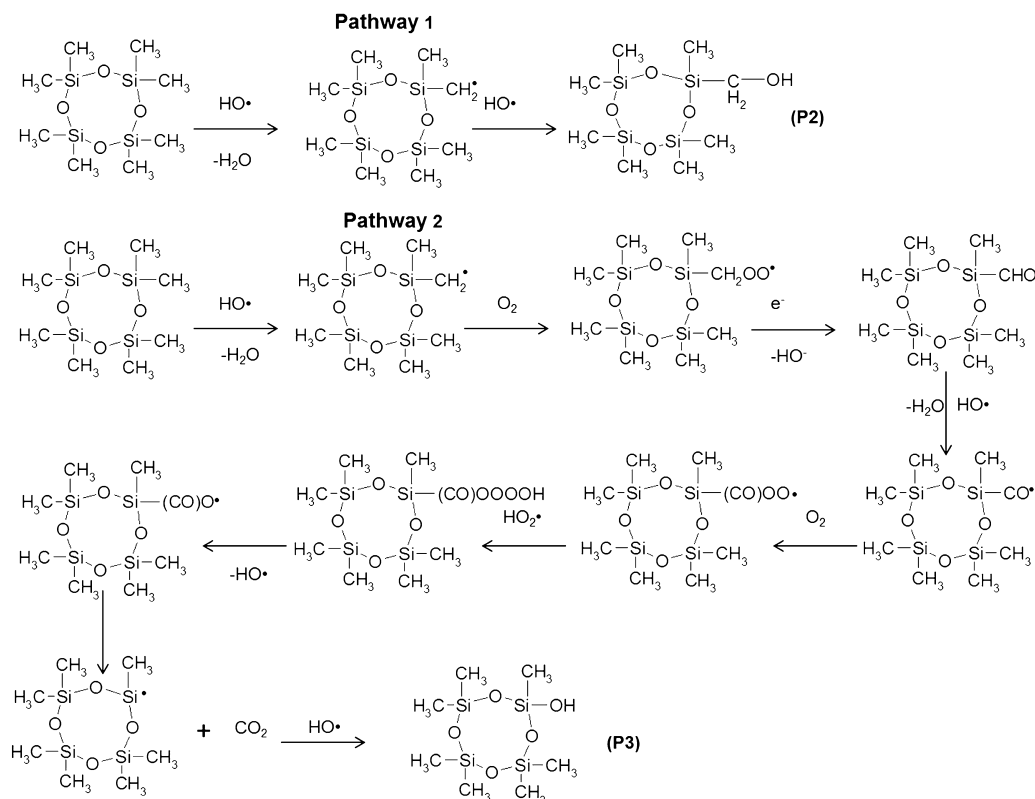


Fig. 7. Tentative mechanism for the photocatalytic oxidation of D4 in gas phase.

of OH. On the other hand, the peak at (B.E. = 529.9 eV) corresponding to TiO_2 decreases significantly after 48 and 72 h. After 72 h of irradiation only the component SiO_2 is present. The results are in agreement with those of $\text{Si}2p$ and can be explained by the formation of an overlayer of intermediate compounds during the PCO on TiO_2 and leading to its deactivation. In addition the presence of OH after 48 h can be attributed to intermediate organic compounds containing OH and after 3 days of irradiation, the adsorbed organic compounds on the TiO_2 surface become progressively oxidized into SiO_2 .

Ambient carbon contamination is always present, and this often complicates analysis of the $\text{C}1s$ peak. In the present work, results of atomic percentages of carbon analyzed by XPS are in line with those obtained with $\text{Si}2p$. The carbon content increases first after 48 h of PCO from 25% to 42% and then decreases to 31% after 3 days.

These results could lead to the conclusion that at 48 h, intermediates are constituted of SiOH and methyl groups (and/or methylene), but after 72 h, SiOH and methyl (and/or methylene) groups are oxidized into SiO_2 .

3.6. Reaction pathways

On the basis of the analysis of TD–GC–MS, APCI and XPS measurements combined with the identification of reaction intermediates and literature data, the first steps of possible photocatalytic degradation pathway of D4 are proposed in Fig. 7.

The first step implies the oxidation of the D4 via HO^\bullet to form an alkyl radical and water. This alkyl radical can react with O_2 or an HO^\bullet radical leading to 2 pathways. In the first one, the alkyl radical reacts with HO^\bullet , to give the intermediate compound identified in phase gas, heptamethyl(hydroxymethyl)cyclotetrasiloxane.

In the second one, as seen in Fig. 7, the alkyl radical reacts with O_2 to produce a peroxy radical attached to D4 as proposed by

Sommerlade et al. [25]. This peroxy radical can gain one electron to form an aldehyde attached to one of the Si of D4. The next step consists in the oxidation of this product by HO^\bullet , then the product formed can be further oxidized by HO_2^\bullet to form a tetraoxide attached to D4, where it decomposes to form radical products ($-\text{Si}-\text{COO}^\bullet$ and HO^\bullet) [27]. Additional decomposition produces $-\text{Si}$ radical and CO_2 while the next step is an oxidation of the silicon radical with HO^\bullet to give heptamethylhydroxycyclotetrasiloxane. The CO_2 formed desorbs and is detected in the gas phase using PDHID analysis while heptamethylhydroxycyclotetrasiloxane seems to remain mainly adsorbed on the surface of the catalyst as was shown in XPS analysis, and only a small amount was found in the gas phase using TD–GC–MS and APCI.

While D3 was identified as an intermediate compound, there is no detailed pathway proposed, but probably a ring opening during the photocatalytic degradation occurred to give linear compounds which can form a ring with the loss of $\text{Si}(\text{CH}_3)\text{OH}$, as Whelan et al. proposed [20].

3.7. Photocatalytic oxidation of D4/Toluene binary mixture

Experiments on a binary mixture made up of D4 and toluene were carried out for a better understanding of the impact of VMS on photocatalytic systems.

As shown in Fig. 8, for mixture A (250 ppbv for each pollutant), toluene conversion reaches 98% in the first hours of the PCO while D4 conversion was ca. 75%. After 12 h of irradiation, the toluene conversion decreases from 98 to 77% and then continues steadily to decrease down to 72 h of irradiation to reach a value of ca. 20%.

The behavior of D4 is different since at the beginning of the experiment a conversion of 75% is reached, but after 24 h the D4 conversion increases. Beyond this time, D4 conversion rate decreases regularly but to a lesser extent with respect to the

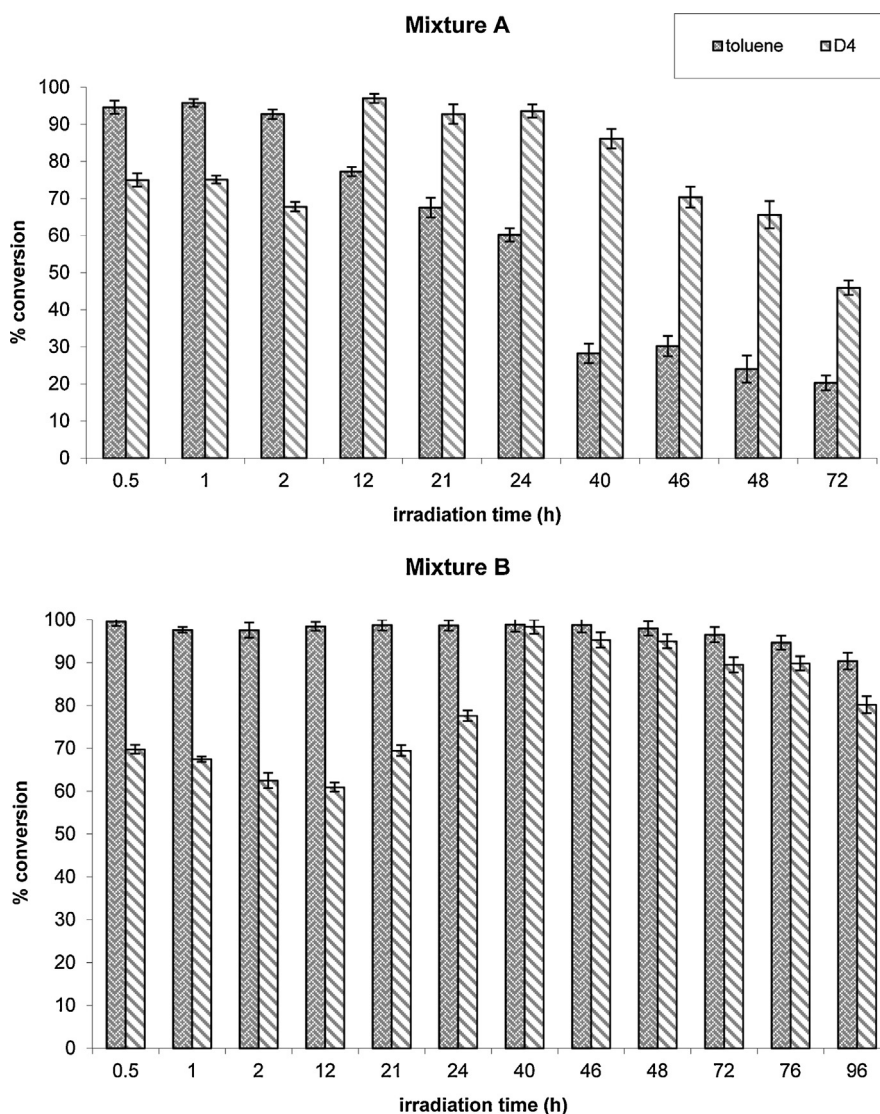


Fig. 8. Influence of conversion (%) of toluene in presence of D4; RH=40% (Mixture A inlet concentration: [D4]=[toluene]=250 ppbv; Mixture B inlet concentration: [D4]=50 ppbv; [toluene]=250 ppbv).

toluene. Intermediate compounds of D4, adsorb on the TiO_2 surface, leading progressively to a decrease in TiO_2 activity.

For mixture B (50 ppbv and 250 ppbv for D4 and toluene, respectively) as shown in Fig. 8, the same trend is observed but to a lesser extent. At the beginning since D4 is less concentrated its conversion is more difficult than in mixture A.

For mixture B, the deactivation of TiO_2 appears after a longer irradiation time.

4. Conclusion

This work illustrates the effect of VMS on photocatalytic systems using D4 as a model compound. It was shown that photocatalytic activity decreased with increasing reaction time. These results were tentatively explained first by the analysis of the gas phase using techniques such as TD-GC-MS, APCI in which three different intermediate organic products were identified viz., heptamethylhydroxycyclotetrasiloxane, heptamethyl(hydroxymethyl) cyclotetrasiloxane and hexamethylcyclotetrasiloxane. Secondly, the TiO_2 surface was also analyzed using XPS and it was found that after 48 h of PCO, a deposit of organic intermediates containing SiOH could be responsible for a partial TiO_2 deactivation while after 72 h the almost total deactivation was due to the formation of SiO_2 .

Experiments on a binary mixture made up of D4 and toluene were also carried out in order to highlight the impact of D4 on photocatalytic systems, and results showed that D4 was responsible for the deactivation of TiO_2 which was revealed by a decrease in photocatalytic activity.

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